Dalton Transactions



COMMUNICATION

View Article Online



Cite this: *Dalton Trans.*, 2016, **45**, 9766

Received 5th February 2016, Accepted 4th March 2016 DOI: 10.1039/c6dt00522e

www.rsc.org/dalton

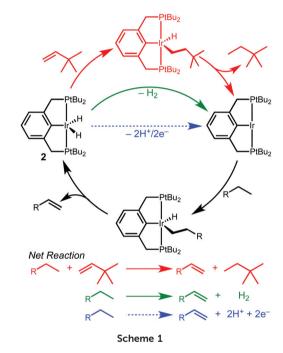
Electrochemical and chemical routes to hydride loss from an iridium dihydride†

A. G. Walden, A. Kumar, b.c N. Lease, A. S. Goldman and A. J. M. Miller*

With a view towards replacing sacrificial hydrogen acceptors in alkane dehydrogenation catalysis, electrochemical methods for oxidative activation of a pincer-ligated iridium hydride intermediate were explored. A 1H⁺/2e⁻ oxidation process was observed in THF solvent, with net hydride loss leading to a reactive cationic intermediate that can be trapped by chloride. Analogous reactivity was observed with the concerted hydride transfer reagent Ph₃C⁺, connecting chemical and electrochemical hydride loss pathways.

Iridium complexes supported by tridentate ^{R_4}PCP ($^{R_4}PCP = \kappa^3$ -C₆H₃-2,6-(CH₂PR₂)₂) pincer ligands are prolific dehydrogenation catalysts, enabling landmark transformations such as the dehydrogenation, 1,2 metathesis, 3 coupling 4,5 and dehydroaromatization of alkanes. Efficient dehydrogenation reactions require a sacrificial hydrogen acceptor, typically an olefin. The hydrogen acceptor alters the overall reaction thermodynamics and activates the iridium dihydride species. In transfer dehydrogenation, catalyst activation occurs by insertion of the sacrificial olefin into one Ir–H bond, followed by C–H bond-forming reductive elimination with the other Ir–H bond, generating a highly reactive $^{14}e^-$ intermediate capable of alkane C–H bond activation (Scheme 1).

The requirement of an added stoichiometric reagent represents a significant limitation in dehydrogenation reactions. In considering new strategies to promote dehydrogenation reactions, we were drawn to electrochemical methods that could *decouple* the catalyst activating and hydrogen accepting steps. We envisioned electrochemical oxidation of (R4PCP)Ir(H)₂ at an anode, generating a catalytic intermediate while releasing 2H⁺/2e⁻ (Scheme 1) that could be used to drive any range of reactions at the cathode.



Electrochemical dehydrogenation relies on (sometimes coupled) electron transfer and proton transfer steps, 13,14 while chemical dehydrogenation often involves concerted hydride transfer. Recent reports have started to draw connections between chemical and electrochemical processes, however. For example, inspired by a report of (^{R_4}PCP)Ir-catalyzed hydrogenation of CO₂ to formate, 17 Brookhart and Meyer developed an analogous electrochemical reduction of CO₂ to formate catalyzed by ($^{tBu_4}POCOP$)Ir complexes ($^{tBu_4}POCOP = \kappa^3$ -C₆H₃-2,6-(OP^tBu₂)₂). A striking oxidative example involves two different catalysts for the same alcohol oxidation reaction that operate by two different mechanisms, either a concerted H₂ loss mechanism or an outer-sphere electron transfer mechanism in which a chemical oxidant (not an electrode) and a base facilitate $2H^+/2e^-$ loss. 21

^aDepartment of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599-3290. USA. F-mail: aimm@email.unc.edu

^bDepartment of Chemistry and Chemical Biology, Rutgers, The State University of New Jersey, New Brunswick, New Jersey 08903, USA

^cDepartment of Chemistry, Indian Institute of Technology Guwahati, Guwahati - 781039. Assam. India

 $[\]dagger$ Electronic supplementary information (ESI) available: Experimental details, electrochemical data, and NMR spectra. See DOI: 10.1039/c6dt00522e

Dalton Transactions Communication

Studies of electrochemical reactions that parallel wellknown organometallic oxidations can help bridge the divide between chemical and electrochemical methods. This report focuses on the oxidation of a pincer-ligated iridium dihydride. Net loss of hydride (H⁺/2e⁻) is promoted by either electrochemical or chemical methods to produce an iridium monohydride species.

The dihydride complex was prepared according to previously reported procedures by dehydrohalogenation of (tBu₄PCP)Ir(H)(Cl) (1) under an H₂ atmosphere. This procedure affords a mixture of the five-coordinate dihydride (tBu4PCP)Ir(H)2 (2) and (tBu4PCP)Ir(H)4 (3).23 Samples could be stirred in pentane, filtered, and dried under vacuum to remove the dihydrogen ligand and provide pure 2.1

The oxidation of dihydride 2 was initially explored using cyclic voltammetry (CV). When a solution of 2 in argon-saturated THF containing [Bu₄N][PF₆] supporting electrolyte was assessed by a CV sweep to oxidative potentials, a single irreversible feature was observed at $-0.08 \text{ V} \text{ vs. Cp}_2\text{Fe}^{+/0}$ (Fig. 1). No return reduction process was apparent, even as the scan rate was increased to 1 V s⁻¹.

An irreversible electrochemical oxidation is consistent with a rapid chemical reaction following electron transfer from 2 to the electrode. The dihydride 2 is more easily oxidized than the hydridochloride complex 1, which exhibited a quasi-reversible oxidation around 0.5 V vs. Cp₂Fe^{+/0} in CH₂Cl₂ at fast scan rates in a prior study.24

To identify the product formed at positive potentials under argon, a controlled potential electrolysis experiment was carried out. A high-surface-area reticulated vitreous carbon working electrode was submersed in a THF solution of dihydride 2 and polarized to 0.2 V vs. Cp₂Fe^{+/0}. The flow of current diminished as a gradual color change from pale orange to pale yellow was observed. The oxidation passed 239 mC of charge, corresponding to 1.9 e per Ir, but an aliquot analyzed by ³¹P{¹H} NMR spectroscopy revealed a mixture of species.

Considering the possibility that oxidation of 2 would produce a reactive cationic species, 25 the oxidative electrochemistry was also carried out in the presence of a chloride ion source as a trapping agent. In the presence of LiCl (and

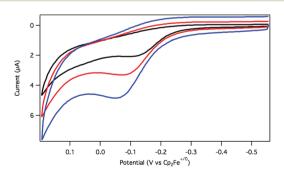


Fig. 1 Cyclic voltammetry of 2 at 25 mV s^{-1} (black), 100 mV s^{-1} (red), and 250 mV s⁻¹ (blue) in THF solution with 0.1 M [Bu₄N][PF₆] electrolyte. Glassy carbon working electrode, platinum counter electrode, Ag wire pseudo-reference electrode, 298 K.

$$\begin{array}{c|c} & [Bu_4N][CI] \\ & THF \ under \ Ar \\ & +0.2 \ V, \ 25 \ ^{\circ}C \\ & -H^{+}/2e^{-} \\ & &$$

with conditions otherwise similar to those described above), the CV response of 2 was essentially unchanged relative to chloride-free conditions, suggesting that chloride does not influence the initial oxidation process.

Controlled potential electrolysis of a THF solution containing 2 and excess LiCl or [Bu₄N][Cl] was conducted at 0.2 V vs. $Cp_2Fe^{+/0}$ (Scheme 2). In the presence of chloride, the solution color changed from pale orange to a much brighter orange, and the 283 mC of charge passed corresponds to a 2e oxidation (2.3 e⁻ per Ir). Analysis by ³¹P{¹H} NMR spectroscopy now revealed a single phosphorous-containing species (δ 69). The product was isolated from the electrolyte by removal of the THF under vacuum and extraction with pentane. Full NMR spectroscopic analysis in THF- d_8 showed a triplet hydride resonance far upfield (δ -42.9) in the ¹H NMR spectrum that is diagnostic of (*Bu4PCP)Ir(H)(Cl) (1). All of the 31P and 1H NMR signals closely matched the previously reported values.²²

The electrochemical conversion of dihydride 2 to hydridochloride 1 represents a net hydride abstraction via the loss of 2e to the anode and loss of H (to solution or perhaps to a surface site on the electrode), followed by chloride binding. This two-step electrochemical-chemical (EC) transformation is consistent with the irreversible CV response (prior studies of (pincer)Ir(H)(Cl) also implicated an EC mechanism, but did not identify a product).²⁴ The stability of the product, hydridochloride 1, towards further oxidation at the potentials applied during electrolysis is critical to the success of the reaction.²⁴

Analogous electrochemical hydride loss via a two-electron/ one-proton oxidative process has been reported for a series of Group 6 complexes of the type $CpM(CO)_3H$ (M = Cr, M, W), ²⁶ which may involve a concerted proton-coupled electron transfer event in the tungsten case.²⁷ In contrast, the Rh analogue (^{tBu}4PCP)Rh(H2), which is best described as a Rh(1) dihydrogen complex,28 does not undergo oxidative hydride loss: reversible 1e oxidation is observed in CH₂Cl₂, and H₂ loss is observed in coordinating solvents.29

To further probe the hydride transfer reactivity, chemical methods that could effect an analogous hydride loss were explored. When dihydride 2 is allowed to react with the hydride abstractor $[Ph_3C][B(C_6F_5)_4]$ in THF- d_8 , the solution changes color from pale orange to pale yellow. NMR spectroscopic monitoring revealed a mixture of products analogous to those observed in the initial electrolysis.

Hydride abstraction was next attempted in the presence of a chloride source. Treatment of dihydride 2 with 1 equiv. [Ph₃C][B(C₆F₅)₄] and 5 equiv. [Bu₄N][Cl] led to a color change from pale orange to a much brighter orange, coinciding with

Dalton Transactions Communication

Scheme 3

Scheme 4

the appearance of the characteristic signals of hydridochloride complex 1 by ³¹P{¹H} and ¹H NMR spectroscopy (Scheme 3). Triphenylmethane is also observed by ¹H NMR spectroscopy, clearly identifying the fate of the hydride.

We suggest that the electrochemical and chemical hydride abstractions proceed via a shared intermediate, given the similar product distributions under various reaction conditions. As shown in Scheme 4, we hypothesize that oxidation of dihydride 2 occurs as a net 1H⁺/2e⁻ process (via one of the pathways described above) to generate a reactive monohydride cation, $\lceil (^{tBu_4}PCP)Ir(H) \rceil^+$ (4). Chemical hydride transfer from 2 to [Ph₃C][B(C₆F₅)₄] would also afford 4. We are not aware of any prior reported isolation of cation 4. An analogous [(tBu4POCOP)Ir(H)] species, isolated as an acetone or dichloromethane adduct, is an active hydrosilylation catalyst. 30,31

From this shared intermediate cation 4, trapping with chloride ion can generate the hydridochloride 1. In the absence of chloride, we suspect that cation 4 decomposes through reactions with itself and/or the solvent, the details of which are currently under investigation. The observation of identical products under electrochemical and chemical reaction conditions suggests that future electrochemical oxidations (even in non-polar solvents)³²⁻³⁴ can be modeled after existing hydride abstraction reactions.

By implicating a key monohydride cation intermediate and building an analogy between well-defined organometallic hydride abstraction reactions and electrochemical oxidation processes, these joint chemical/electrochemical studies provide a foundation for future development of electrochemical dehydrogenation processes.

Acknowledgements

The authors acknowledge funding from NSF Center for Enabling New Technologies through Catalysis (CENTC), CHE-1205189. The Templeton group generously provided access to an argon-filled glovebox.

Notes and references

‡ Solutions containing hydrides 2 and 3 are stable under Ar or H2, but decompose under N2 or air to a mixture of products with distinct electrochemical responses.35

- 1 M. Gupta, C. Hagen, R. J. Flesher, W. C. Kaska and C. M. Jensen, Chem. Commun., 1996, 2083-2084.
- 2 A. Kumar, T. Zhou, T. J. Emge, O. Mironov, R. J. Saxton, K. Krogh-Jespersen and A. S. Goldman, J. Am. Chem. Soc., 2015, 137, 9894-9911.
- 3 A. S. Goldman, A. H. Roy, Z. Huang, R. Ahuja, W. Schinski and M. Brookhart, Science, 2006, 312, 257-261.
- 4 D. C. Leitch, Y. C. Lam, J. A. Labinger and J. E. Bercaw, J. Am. Chem. Soc., 2013, 135, 10302-10305.
- 5 J. A. Labinger, D. C. Leitch, J. E. Bercaw, M. A. Deimund and M. E. Davis, Top. Catal., 2015, 58, 494-501.
- 6 R. Ahuja, B. Punji, M. Findlater, C. Supplee, W. Schinski, M. Brookhart and A. S. Goldman, Nat. Chem., 2011, 3, 167-171.
- 7 J. Choi, A. H. Roy MacArthur, M. Brookhart and A. S. Goldman, Chem. Rev., 2011, 111, 1761-1779.
- 8 K. Krogh-Jespersen, M. Czerw, N. Summa, K. B. Renkema, P. D. Achord and A. S. Goldman, J. Am. Chem. Soc., 2002, **124**, 11404-11416.
- 9 K. B. Renkema, Y. V. Kissin and A. S. Goldman, J. Am. Chem. Soc., 2003, 125, 7770-7771.
- 10 W. Xu, G. P. Rosini, K. Krogh-Jespersen, A. S. Goldman, M. Gupta, C. M. Jensen and W. C. Kaska, Chem. Commun., 1997, 2273-2274.
- 11 P. Driscoll, E. Deunf, L. Rubin, O. Luca, R. H. Crabtree, C. Chidsey, J. Arnold and J. Kerr, ECS Trans., 2011, 35, 3-17.
- 12 B. Rausch, M. D. Symes and L. Cronin, J. Am. Chem. Soc., 2013, 135, 13656-13659.
- 13 C. Costentin, M. Robert and J.-M. Savéant, Chem. Rev., 2010, 110, PR1-PR40.
- 14 D. R. Weinberg, C. J. Gagliardi, J. F. Hull, C. F. Murphy, C. A. Kent, B. C. Westlake, A. Paul, D. H. Ess, D. G. McCafferty and T. J. Meyer, Chem. Rev., 2012, 112, 4016-4093.
- 15 S. E. Clapham, A. Hadzovic and R. H. Morris, Coord. Chem. Rev., 2004, 248, 2201-2237.
- 16 C. R. Waidmann, A. J. M. Miller, C.-W. A. Ng, M. L. Scheuermann, T. R. Porter, T. A. Tronic and J. M. Mayer, Energy Environ. Sci., 2012, 5, 7771-7780.
- 17 R. Tanaka, M. Yamashita and K. Nozaki, J. Am. Chem. Soc., 2009, 131, 14168-14169.
- 18 P. Kang, C. Cheng, Z. Chen, C. K. Schauer, T. J. Meyer and M. Brookhart, J. Am. Chem. Soc., 2012, 134, 5500-5503.
- 19 P. Kang, T. J. Meyer and M. Brookhart, Chem. Sci., 2013, 4, 3497-3502.
- 20 P. Kang, S. Zhang, T. J. Meyer and M. Brookhart, Angew. Chem., Int. Ed., 2014, 53, 8709-8713.
- 21 P. J. Bonitatibus, S. Chakraborty, M. D. Doherty, O. Siclovan, W. D. Jones and G. L. Soloveichik, Proc. Natl. Acad. Sci. U. S. A., 2015, 112, 1687-1692.

Dalton Transactions Communication

- 22 C. J. Moulton and B. L. Shaw, J. Chem. Soc., Dalton Trans., 1976, 1020–1024.
- 23 T. J. Hebden, K. I. Goldberg, D. M. Heinekey, X. Zhang, T. J. Emge, A. S. Goldman and K. Krogh-Jespersen, *Inorg. Chem.*, 2010, 49, 1733–1742.
- 24 F. Novak, B. Speiser, H. A. Y. Mohammad and H. A. Mayer, *Electrochim. Acta*, 2004, **49**, 3841–3853.
- 25 M. Gupta, W. C. Kaska and C. M. Jensen, *Chem. Commun.*, 1997, 461–462.
- 26 O. B. Ryan, M. Tilset and V. D. Parker, *J. Am. Chem. Soc.*, 1990, 112, 2618–2626.
- 27 M. Bourrez, R. Steinmetz, S. Ott, F. Gloaguen and L. Hammarström, *Nat. Chem.*, 2015, 7, 140–145.
- 28 K. Huang, J. H. Han, C. B. Musgrave and E. Fujita, *Organometallics*, 2007, **26**, 508–513.

- 29 M. D. Doherty, S. J. Konezny, V. S. Batista and G. L. Soloveichik, *J. Organomet. Chem.*, 2014, 762, 94–97.
- 30 J. Yang and M. Brookhart, J. Am. Chem. Soc., 2007, 129, 12656-12657.
- 31 J. Yang and M. Brookhart, *Adv. Synth. Catal.*, 2009, **351**, 175–187.
- 32 W. E. Geiger and F. Barrière, *Acc. Chem. Res.*, 2010, 43, 1030–1039.
- 33 R. J. LeSuer, C. Buttolph and W. E. Geiger, *Anal. Chem.*, 2004, **76**, 6395–6401.
- 34 A. P. Abbott and D. J. Schiffrin, J. Chem. Soc., Faraday Trans., 1990, 86, 1453–1459.
- 35 R. Ghosh, M. Kanzelberger, T. J. Emge, G. S. Hall and A. S. Goldman, *Organometallics*, 2006, 25, 5668–5671.